



Use of an Atmospheric Atomic Oxygen Beam for Restoration of Defaced Paintings

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Summary

An atmospheric atomic oxygen beam has been found to be effective in removing organic materials through oxidation that are typical of graffiti or other contaminant defacements which may occur to the surfaces of paintings. The technique, developed by the National Aeronautics and Space Administration, is portable and was successfully used at the Carnegie Museum of Art to remove a lipstick smudge from the surface of porous paint on the Andy Warhol painting "Bathtub." This process was also evaluated for suitability to remove felt tip and ball point ink graffiti from paper, gesso on canvas and cotton canvas.

Introduction

NASA Glenn Research Center has been investigating the effects of atomic oxygen interaction with materials as a result of the interest in understanding materials degradation on spacecraft in low Earth orbit where atomic oxygen is the most predominant specie. Atomic oxygen is formed in low Earth orbit through photodissociation of atmospheric diatomic oxygen by means of ultraviolet radiation from the sun. All hydrocarbon materials exposed to atomic oxygen oxidize to form volatile oxidation products resulting in a gradual loss of thickness of the hydrocarbon material (Banks and Rutledge, 1988). As a result of NASA's need to be able to simulate the atomic oxygen found in the low Earth orbital environment, numerous facilities have been constructed which produce atomic oxygen in a low-pressure environment. Exposure of a wide variety of materials to thermal energy atomic oxygen plasmas in these facilities has resulted in an awareness that such atomic oxygen may be useful for removing organic contaminants such as soot or aged varnishes from the surfaces of paintings (Rutledge, Banks and Cales, 1994), (Rutledge, et al, 1998). As a result of several art conservators inquiries as to whether the atomic oxygen cleaning process could be conducted at atmospheric pressure without requiring the use of a vacuum facility, an atmospheric atomic oxygen beam cleaning system was developed (Banks, Rutledge and Norris, 1998), (Banks and Rutledge, 1997).

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The atmospheric atomic oxygen source uses an electric arc to dissociate O_2 molecules in an environment that is rich in helium content. The atomic oxygen formed is inhibited from recombining back into O_2 by the presence of a high concentration of helium (see fig. 1). The arc forms between an anode needle and a cathode orifice plate in the presence of the helium-oxygen mixture. A cathode orifice plate is negatively biased such that it attracts positive atomic oxygen ions formed in the arc. However, the arc is blown through the orifice resulting in a stream of oxygen ions and charge exchange oxygen neutrals being propelled downstream for a distance of ~1 cm. These atomic oxygen species can then react at atmospheric pressure with organic or polymeric materials exposed to the beam.

An Andy Warhol painting (Bathtub, 1961) was defaced in September of 1997 as a result of someone kissing the painting while wearing lipstick. The lipstick had been handed out during a cosmetics celebration held at the Andy Warhol Museum, where the painting was located. The red lipstick imprint was highly visible on the painting surface that consisted of a very dry, cream-colored matte-finish oil paint. Conservators at the Carnegie Museum of Art, responsible for the Andy Warhol Museum collection, felt that the porous texture of the painting surface would not allow the satisfactory removal of the lipstick by use of conventional solvent techniques. As a result of their awareness of the atmospheric atomic oxygen beam cleaning technique, collaborative efforts were initiated with the NASA Glenn Research Center to attempt to use the technique to remove the lipstick accretion.

Conservator inquiries about the feasibility of using the atmospheric atomic oxygen beam to remove other types of defacement such as pen marks has also prompted the exploration of its ability to remove felt tip and ball point pen marks on paper, gesso coated canvas and cotton canvas.

Apparatus and Procedures

A schematic diagram of the atmospheric atomic oxygen source is shown below in figure 2. The arc is powered by a 7 kV DC power supply with a 1 M Ω current limiting resistor. These are used to create an arc current of 5.8 mA to produce the atomic oxygen beam. A faint glow indicating the evidence of the atomic oxygen beam can be seen emerging from the cathode orifice plate which is in the shape of a truncated cone (see fig. 3). The cathode orifice plate is 0.254 mm thick 300 series stainless steel with a 3.175 mm diameter orifice through it for the arc pass through. The anode needle is sharpened tungsten with its tip located 1.6 mm upstream of the anode orifice plate. The painting surface was arranged to be 8 mm downstream of the cathode orifice resulting in an atomic oxygen beam cleaning area 3 to 5 mm in diameter. To assure adequate overlap of cleaned spots on the lipstick smudge, the atomic oxygen beam was translated only 1.6 mm at a time in both the horizontal and vertical direction until all visible signs of lipstick were removed.

The portable configuration of the atmospheric atomic oxygen beam system including the power supply and load resistor, as configured to remove the lipstick smudge from the Andy Warhol painting "Bathtub," is shown in figure 4. Because the atomic oxygen beam does generate a small amount of ozone, the beam system and the painting were located in front of a fume hood (see fig. 4). The gas feed through arc system consisted of an oxygen flow of 0.1 to 0.2 L/min mixed with a helium flow rate of 4.3 L/min.

The atomic oxygen cleaning was first conducted on mock-ups using a variety of manufacturers' lipsticks, including the one thought to be the defacement smudge (Eva Szabo Shade 302 Coral, distributed in Pittsburgh, Pa.). Initial tests indicated that the amount of time required to remove the lipstick could be significantly reduced by first removing as much of the lipstick as possible with solvents. The lipstick smudge on the painting was first cleaned using a cotton swab which was dipped in 1 part by volume of acetone and 3 parts by volume benzene. The swab was then used to wipe off as much of the lipstick as possible. The atomic oxygen beam was then applied in an incrementally rastered manner to oxidize the remaining lipstick smudge. After atomic oxygen cleaning, a portion of the lipstick smudge was then treated with a Groomstick[®] to see if a total reduction in visibility of lipstick would occur. However, underlying lipstick which was transported through the porous paint, either by mechanical or solvent means caused the visibility to actually increase. As a result of these tests, the procedure was modified such that the atomic oxygen cleaning was not followed by Groomstick[®] cleaning.

The atmospheric atomic oxygen source was also used to evaluate the effectiveness of using it to remove ball point ink and felt tip pen marks from 25 percent cotton fiber paper, acrylic gesso on canvas, and cotton canvas. The atomic oxygen beam system configuration and operating conditions used for oxidizing the pen marks was identical to that used for removing the lipstick smudge with the exception that the duration was changed as necessary to attempt to remove the ink marks while minimizing undesirable excess oxidation of the underlying organic substrate material.

Results and Discussion

Lipstick Removal

Trials were conducted using atomic oxygen beams to clean a variety of lipstick types from gesso surfaces to assure the cleaning would be satisfactory while not placing a painting at risk due to effects of the beam. All brands of lipstick tested on gesso canvas were found to be adequately cleaned by the atomic oxygen beam. The atmospheric atomic oxygen beam does produce some heating of surfaces exposed to it. As electrically configured in figure 2, an estimated 1200 V potential drop in the arc produces 6.96 W of Joule heating. Some of this heat is carried away through thermal conduction associated with the cathode orifice plate and anode needle. However, a portion of the arc power results in heating the helium and oxygen which is transported to the painting surface. Based on preliminary tests conducted using this configuration, surface temperatures at the painting could range between 77 to 82 °C. Tests were conducted to allow pre-cooling of the gases prior to their passing through the arc site by means of cooling the arc chamber which holds the anode needle and cathode orifice plate. Although no attempt to cool the arc was used for cleaning the Andy Warhol painting, these tests were successful in indicating the feasibility of obtaining a room temperature atomic oxygen beam with suitable arc chamber cooling.

After the cleaning procedure was optimized, the atomic oxygen beam apparatus was configured to be portable and transported to the Carnegie Museum of Art in Pittsburgh, Pa. A photograph of Andy Warhol's painting "Bathtub" is shown in figure 5. The lipstick smudge covered an area ~3.5 cm wide × 3.3 cm high. Tests were first conducted on small amounts of the lipstick applied to the tacking margins of the painting, which exhibited the same white paint substrate as the design surface itself. Since tests on the mock-ups had indicated that preliminary solvent cleaning could significantly reduce time and exposure during the atomic oxygen cleaning phase, the tests on the tacking margins were also done in this way, using a small swab slightly moistened with acetone:benzine 1:3. The atomic oxygen test cleaning succeeded in removing the lipstick, and also apparently removed a thin layer of accumulated grime, exposing a significantly whiter substrate than the surrounding paint. Initial tests suggested that the cleaned area could be adjusted with small amounts of watercolor to match the grime-covered surroundings.

The method described above was then applied to the actual lipstick accretion on the front of the painting, starting first with a small area on the lower lip imprint. After a preliminary solvent cleaning, taking care not to drive solubilized lipstick into the porous paint, the lower lip imprint was cleaned by means of incremental atomic oxygen exposure over the entire lower lip imprint until it appeared free of visible red color. The application of Groomstick® to the lower lip imprint after atomic oxygen beam cleaning removed the oxidized surface of the accretion and enabled underlying remnants of the lipstick oils and dyes to faintly reappear. This result was different from previous trials on experiment samples in which the same lipstick had been applied to gesso canvas and removed by the atomic oxygen beam. The difference between the previous experiments and the actual painting may have been the result of a combination of greater porosity associated with the very dry, porous, cream oil paint of the Andy Warhol painting surface as compared with the more dense acrylic gesso on the trial surfaces, or differences in the pressure by which the kiss was applied to the test samples in comparison with the Andy Warhol painting surface. As a result of the slight re-emergence of the lipstick remnant stains upon use of the Groomstick®, it was decided to reclean the area and refrain from further use of the Groomstick® after atomic oxygen cleaning. The lower lip and upper lip imprints were cleaned in an incrementally rastering manner requiring 5 hr and 25 min of atomic oxygen cleaning to satisfactorily remove all evidence of the lipstick smudge.

Photographs showing the lipstick imprint on the Andy Warhol painting, "Bathtub 1961" can be seen in figure 6(a), which shows the smudge prior to atomic oxygen beam cleaning and figure 6(b) showing the same location after atomic oxygen beam cleaning. As can be seen in figure 6, the lipstick smudge was removed, however, a slight lightening of the entire exposed area resulted. This lightening is thought to be due to a combination of two causes, the first cause being atomic oxygen removal of surface grime as stated above. The second cause of lightening may have been a combination of atomic oxygen bleaching of the paint pigments and oxidation of the organic content of the paint resulting in a more diffusely reflecting surface.

As a result of the atomic oxygen beam cleaning, the painting surface was free of all waxes and oils, thus allowing final color matching restoration to be accomplished. The first step in color matching was to adjust the diffuse reflectance of the cleaned area. After testing several resins on the test cleaned areas on the tacking margins, this was accomplished using a dilute solution of Aquazol® resin in distilled water, matted down with fumed silica. The restoration of the correct color was evaluated on test samples on the perimeter of the painting on the back of the stretcher to identify a suitable color matching technique. The lighter cleaned area was then toned by using a nearly dry watercolor brush to apply a very light gray color to darken the cleaned area

and match the rest of the painting. The applied watercolor paint was then smudged slightly with a cotton swab to adjust the texture to match the surrounding area. This in-painting created a surface appearance in keeping with the surrounding paint, all but eliminating any trace of the lipstick defacement and the lightening caused by the atomic oxygen cleaning. The painting has since been returned to display in the Andy Warhol Museum.

Ink Removal

Atomic oxygen beam cleaning of ink marks from paper, acrylic gesso coated canvas and cotton canvas was found to be practical for some inks and impractical for others (see fig. 7). Atomic oxygen beam exposure durations required to remove ink varied from 4.5 to 12 min for those inks that were oxidizable. Black ink from a Sanford Sharpie® permanent marker was the only type of ink that was not removed by atomic oxygen. This is probably a result of some inks having inorganic pigments which would not oxidize readily.

The atomic oxygen beam did cause some oxidative thinning of paper on both sides of the ink marks. A masking technique was evaluated in which a 0.127 mm thick polyimide Kapton® shield was used to prevent oxidation beyond the pen marks to minimize damage to the unmarked substrate materials. The polyimide shield was used on either side of the pen mark lines in much the same way an erasure shield is used. The Kapton® shield was found to be effective to minimize oxidation of the paper beyond the ink marks. Without use of the shield, some thinning of the paper was evident upon holding the paper up to allow light to pass through.

Conclusions

An atmospheric atomic oxygen beam was used to remove a lipstick smudge from the surface of the Andy Warhol painting "Bathtub." Because lipstick contains oils and waxes, and the surface of the particular painting was highly porous, conventional solvent removal methods were not thought to be feasible approaches to restoration. The atomic oxygen exposure was found to completely remove all oils and greases from the surface of the painting as well as any visible presence of red color pigment. Restoration of the defaced area approximately 3.5 × 3.3 cm high required a total atomic oxygen cleaning duration of 5 hr and 25 min. The resulting cleaned area was slightly lighter than the surrounding cream colored paint, thus requiring restoration of the color to match the surrounding area. This was accomplished by the application a fumed silica filled resin followed by light gray watercolor paint applied with a dry brush and smudging the paint with a cotton swab. The resulting restoration blended well with the surrounding area and the painting was returned to display. Atmospheric atomic oxygen beam cleaning appears useful when no viable alternatives exist. However, consideration should be given to the potential consequences of surface oxidation.

An atmospheric atomic oxygen beam was found useful in removing some types of felt tip pen and ball point pen ink marks from paper, gesso and cotton fabric. Cleaning durations of ~5 to 7 min were required to remove evidence of ink marks that were amenable to oxidation. The use of a polyimide Kapton® shield on both sides of the ink marks minimized loss of paper thickness due to oxidation.

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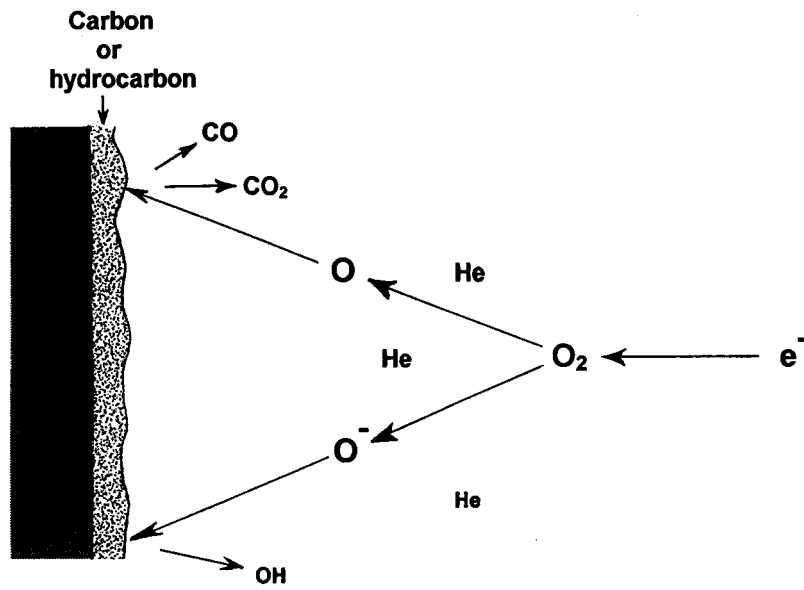


Figure 1.—Atmospheric atomic oxygen production process.

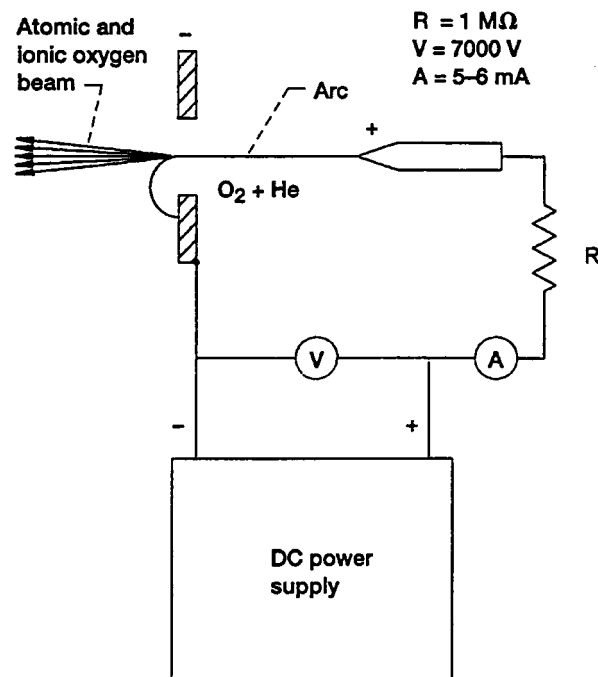


Figure 2.—Schematic diagram of atmospheric atomic oxygen beam system.

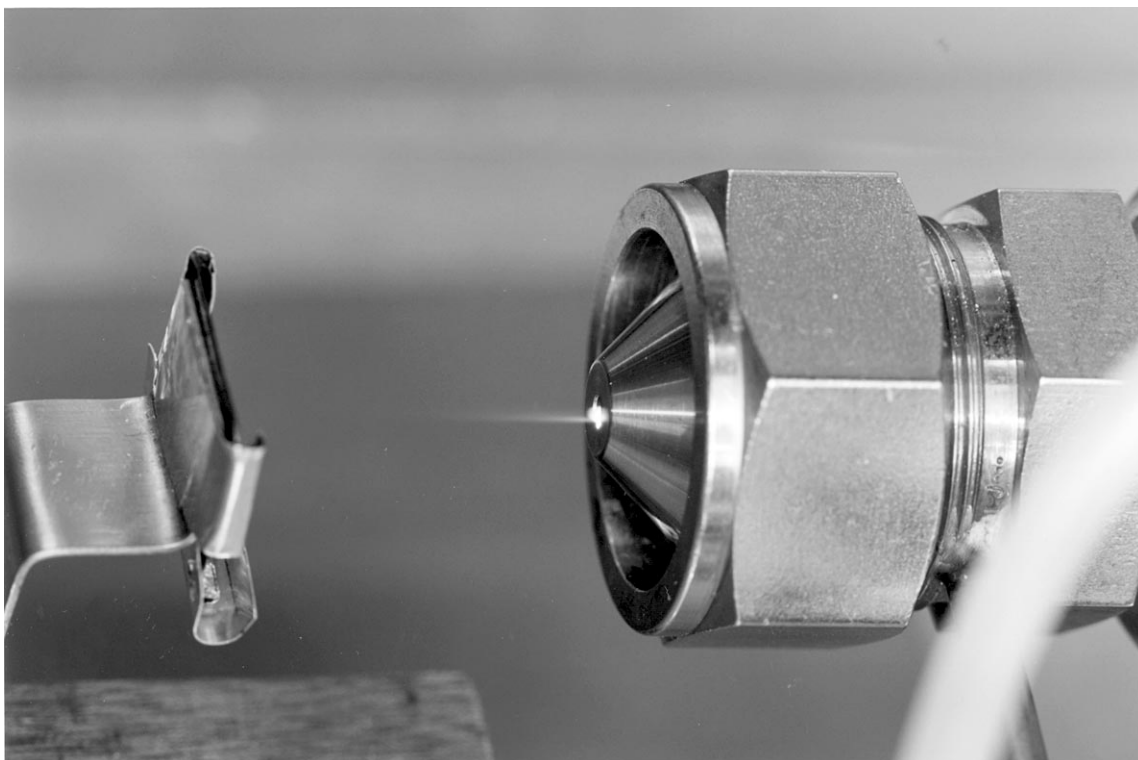


Figure 3.—Close up photograph of atmospheric atomic oxygen beam exiting the cathode orifice.



Figure 4.—Photograph of atmospheric atomic oxygen beam system being used at the Carnegie Museum of Art to clean a lipstick smudge on Andy Warhol's painting "Bathtub" .

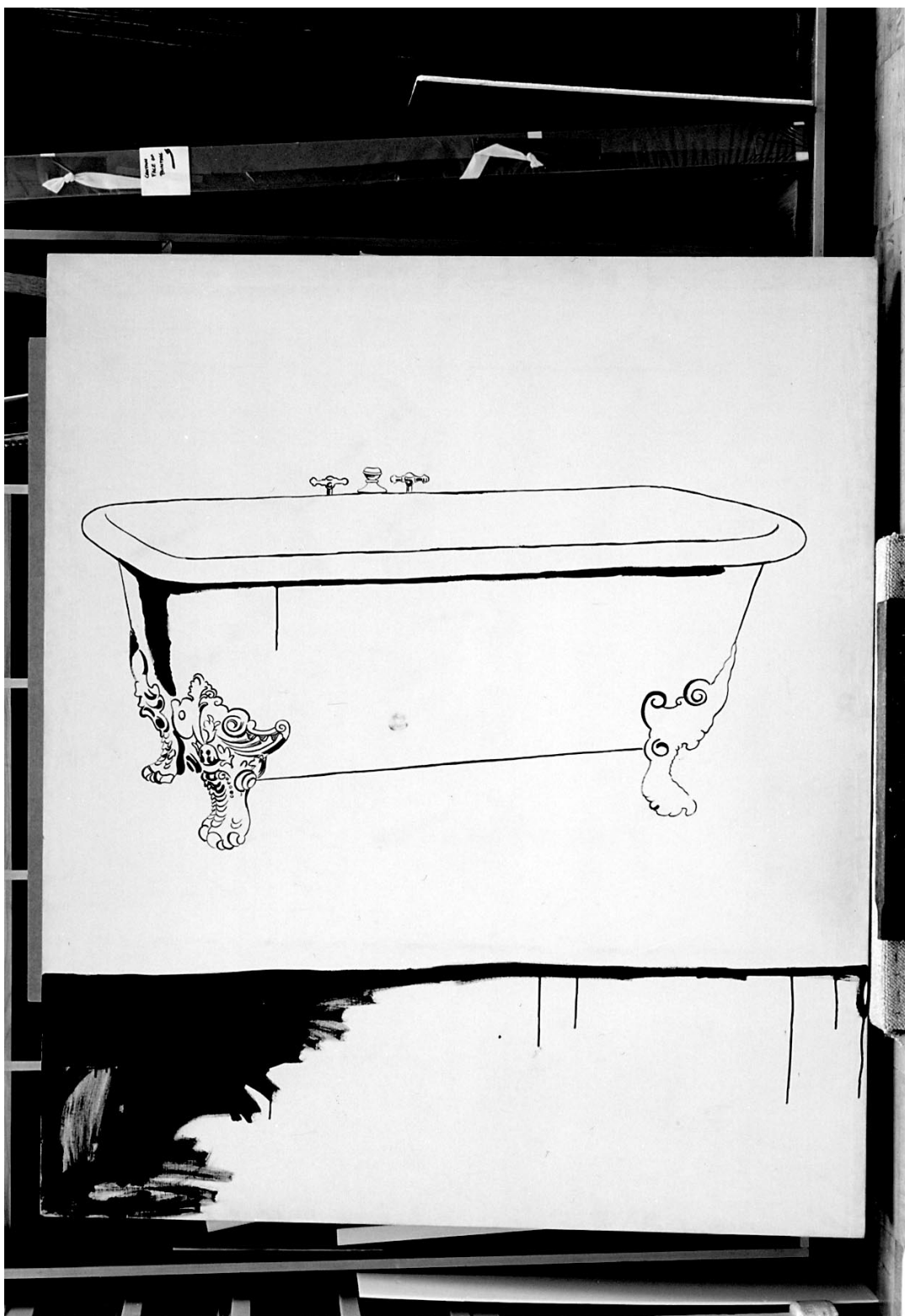


Figure 5.—Photograph of Andy Warhol's painting "Bathtub" with lipstick smudge in central area.

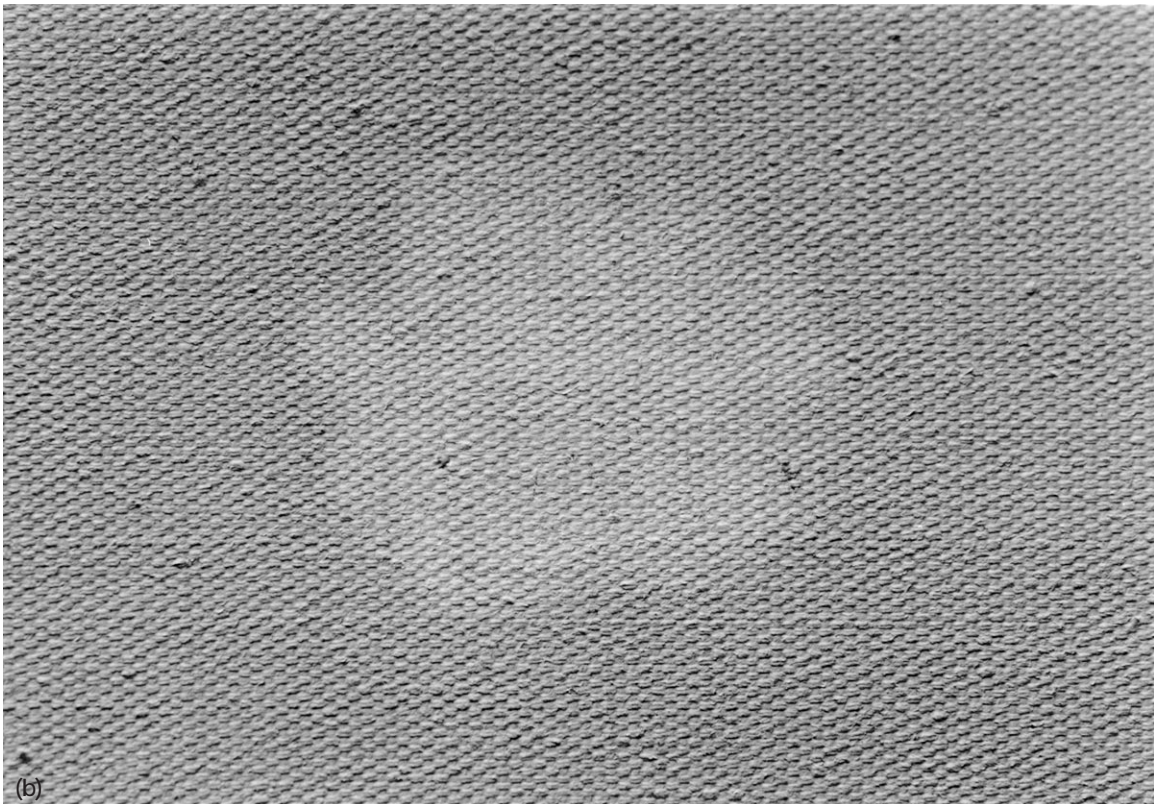
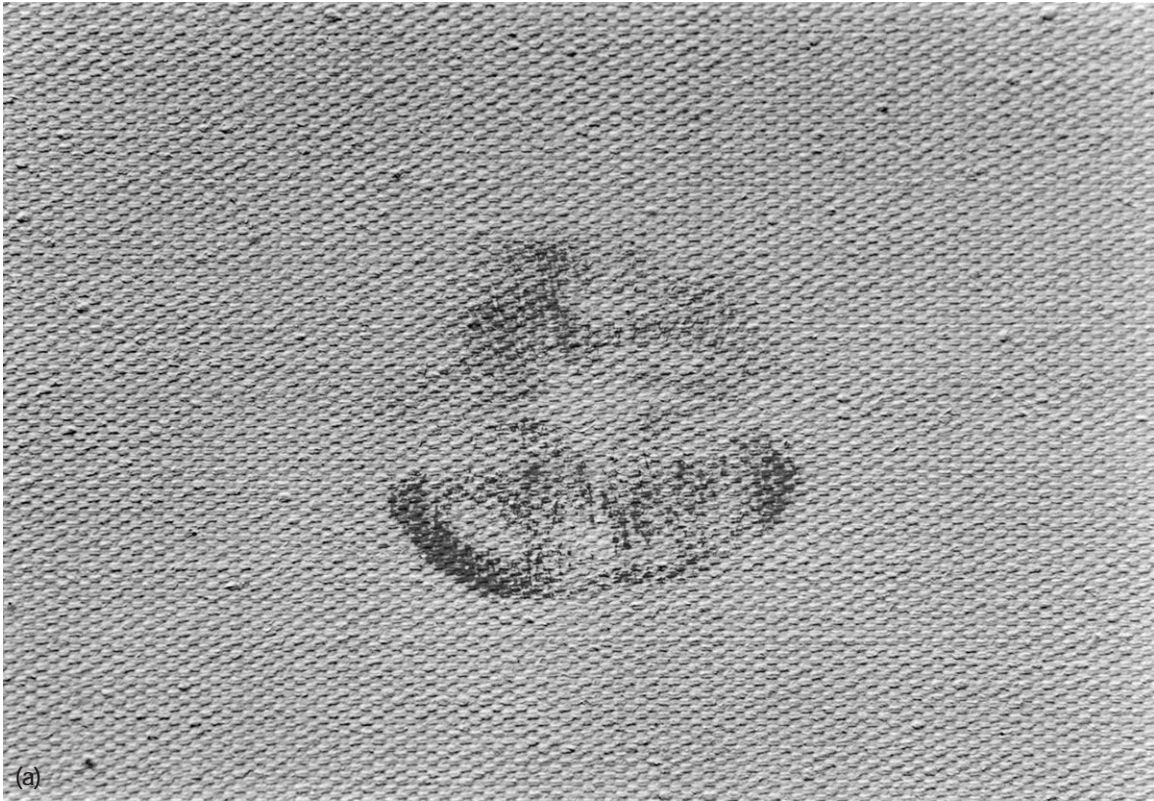
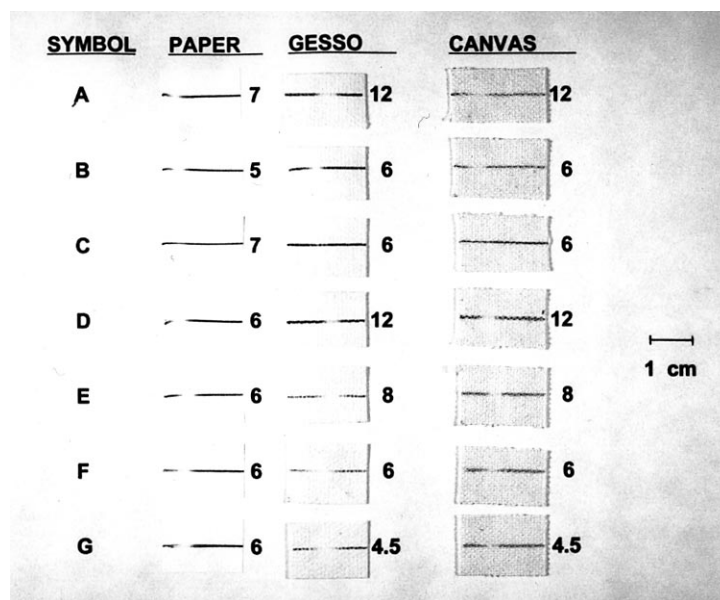


Figure 6.—Close up photograph of lipstick smudge on Andy Warhol's painting "Bathtub". (a) Before atomic oxygen beam cleaning. (b) After atomic oxygen beam cleaning.



KEY:

SYMBOL	DESCRIPTION OF PEN AND INK COLOR
A	American™ Hardpoint, felt tip, black (Eberhard Faber)
B	Waterbury®, felt tip, blue
C	Sanford Sharpie®, Permanent Marker, felt tip, black
D	Paper Mate® Flair®, felt tip, black
E	Bic® Round stic, ballpoint, medium, black
F	Scripto® Stick Pen, ballpoint, medium, blue
G	Paper Mate® Rubberstik, ballpoint, medium, black

Figure 7.—Atomic oxygen beam cleaned pen marks (the gap in the pen mark is the cleaned area) and duration of cleaning in minutes for ink marks on 25% cotton fiber paper, acrylic gesso on canvas and cotton canvas.

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